

CHAPTER III

RESULT AND DISCUSSION

3.1. Synthesis of poly(3-alkylthiophene)

P3HT was obtained as a black solid and was soluble in most common organic solvents such as chloroform, toluene and THF. From ^1H NMR spectrum (CDCl_3) (Figure 3.1), it showed the characteristic hexyl signals including the $-\text{CH}_3$ at δ 0.91 ppm, $-(\text{CH}_2)_4$ at δ 1.2-1.8 ppm and the α -protons from two different regioregularities, HT and HH, at δ 2.79 and 2.56 ppm, respectively. The aromatic protons of thiophene rings from four environments appeared as four resonances between δ 6.98-7.05 ppm. (Figure A-1, Appendix A)

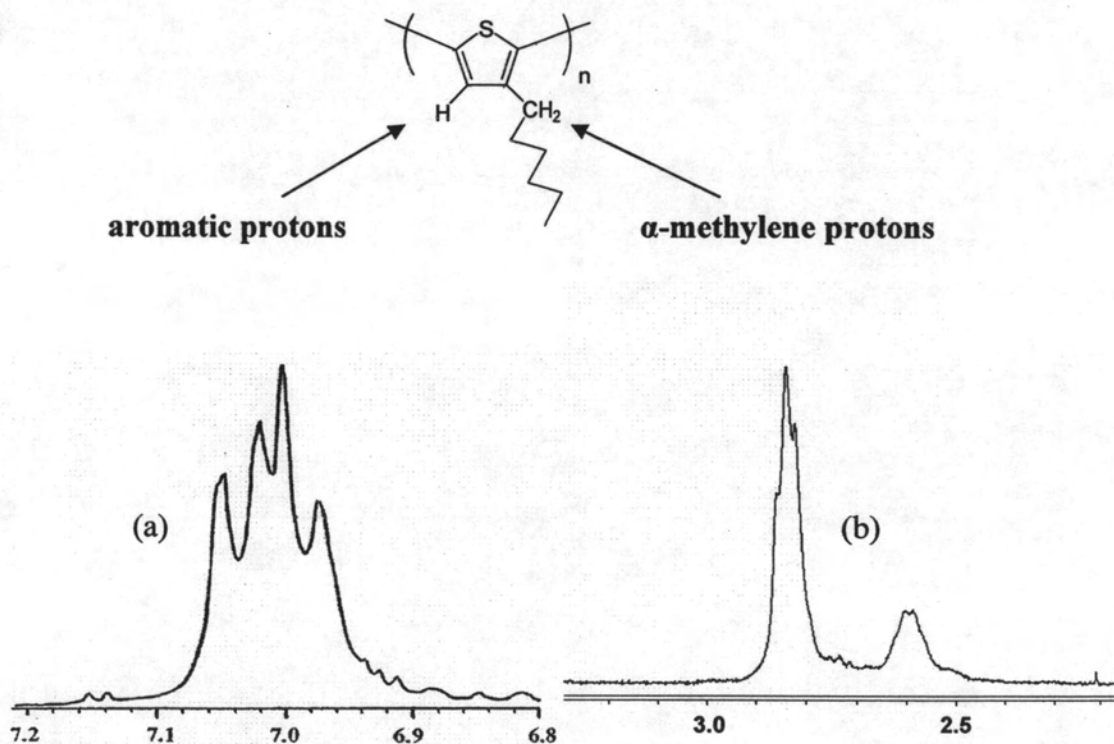


Figure 3.1 Part of ^1H -NMR spectrum of P3HT showing (a) aromatic protons and (b) α -methylene protons.

3.1.1 Effect of mole ratios of 3-hexylthiophene to anhydrous ferric chloride

The %yield of P3HT, prepared from various mole ratios of starting materials according to **Table 2.1**, were found to increase with the amount of anhydrous ferric chloride. This result suggested that the oxidative coupling polymerization became more efficient and complete with higher ratio of the oxidizing agent. Running the reaction at the mole ratio of 3-hexylthiophene to ferric chloride that equals 1:3 was the best condition to obtain the polymer as much as 94% yield with number average molecular weight (M_n) of 20,018 (PDI=3.35, **Figure A-2**, Appendix A) and 78%HT regiocoupling (**Table 3.1**). More ferric chloride did not appear to increase the yield and %HT of the product. Instead, %HT of the polymer tended to decrease. Probably because the faster reaction induced by more reagent resulted in the lower selectivity on the connections among monomers. (%HT values were obtained from ^1H NMR data, See Appendix B for details)

The position and intensity of the absorbance at λ_{max} are generally the characteristic information that can be correlated to some properties of the molecule. In conjugated polymers the λ_{max} values would reflect the chromophore of the regions within the polymer that are mostly present, which would, in turn, contribute most significantly to the macroscopic properties of the polymer. From the experiment, however, λ_{max} values were not much different among the results from various ratios of oxidizing agent (**Figure A-3**, Appendix A). Moreover M_n value of the polymer increased to the maximum at mole ratio of 3-hexylthiophene to ferric chloride that equals 1:3 and seemed to become lower with more oxidizing agent. This result suggested that at first, increasing the ratio of oxidizing agent (1.66 to 2.33) initiated more efficient and complete reaction that gave the longer chain polymer. Although in the case of larger excess of oxidizing agent (more than 3), the higher rate of initiation gave larger numbers of polymer chain but with shortened length.

Table 3.1 Effect of mole ratios of starting materials in the synthesis of P3HT

Mole ratios of 3-hexylthiophene:FeCl ₃	Properties of the P3HT			
	%yield	%HT	λ_{\max}	M_n
1 : 1.66	50	79	433	13,073
1 : 2.33	73	78	439	16,951
1 : 3.00	94	78	440	20,018
1 : 3.66	94	75	431	13,967

3.1.2 Effect of reaction temperature

The tendency of the %yield obtained from the reactions running at -22 °C was quite similar, though in lower numbers than those obtained at room temperature. The mole ratio of 3-hexylthiophene to ferric chloride that equals 1:3 was still considered the best condition giving the highest yield of 88% (Table 3.2). The yield of the product seemed to level off with more ferric chloride. Within the same period of reaction time, the slower rate of the reaction due to lower temperature might cause incomplete reaction, resulting in lower number of %yield comparing to that obtained from the reaction at room temperature. Nevertheless, %HT were at higher values than those from reactions at room temperature in all 3-hexylthiophene to ferric chloride ratios. It is possible that when the rate of the reactions decreased, the monomer became more selective and tended to couple among themselves in the lowest steric fashion, the head-to-tail coupling.

Table 3.2 Synthesis of P3HT at -22 °C

Mole ratios of 3-hexylthiophene:FeCl ₃	Properties of the P3HT			
	%yield	%HT	λ_{\max}	M_n
1 : 1.66	38	88	440	27,105
1 : 2.33	61	80	441	38,345
1 : 3.00	88	81	439	19,146
1 : 3.66	87	78	439	18,036

The λ_{max} value of every ratio was about 440 nm (Figure A-4, Appendix A), indicating no significant difference in their chromophores. The M_n values were mostly found to be much higher than the synthesis at room temperature, especially at lower ratios of the oxidizing agent. The maximum value of M_n (38,345) (Figure A-5, Appendix A) was obtained when running the reaction with the mole ratio of 3-hexylthiophene to ferric chloride that equals 1:2.33. Shorter P3HT chains were obtained at the higher mole ratios but at comparable or a little better than the results from room temperature. It is assumed that much less initiation occurred at low temperature and the polymer grew in length, rather than in numbers of chain. The trade off is the incomplete reaction and lower %yield.

At high reaction temperature (61 °C), the soluble crude product obtained from the reaction showed no signal in the $^1\text{H-NMR}$ spectrum, that corresponded to the structure of P3HT. It was possible that such higher temperature was not suitable for the polymerization reaction because the monomer, reagent or the growing oligomer or polymer were decomposed into insoluble material or other uncharacterizable products.

At much lower temperature (-50 °C), the yield of the polymer was only 7%, further support the previous suggestion that the rate of the reactions dramatically decreased when the reaction temperature decreased. The reaction was incomplete and most of the monomers were still left unreacted.

3.1.3 Effect of the initial concentration of 3-hexylthiophene

In principle, the dilution of monomer solution could lower rate of polymerization reaction that results in higher selectivity, albeit with lower yield. From this current experiment, however, it was found that, the dilution of monomer did not affect the yield, %HT and λ_{max} values of the polymer obtained from various initial concentration of 3-hexylthiophene monomer (Table 3.3). Although the M_n value from the reaction at higher dilution of monomer seemed to become higher. The dilution effect probably gave less initiators and the polymer grew in length rather than in numbers, similar to the result obtained when running reactions at low temperature discussed earlier.

Table 3.3 Synthesis of P3HT from various initial concentration of 3-hexylthiophene

concentration of 3-hexylthiophene (mol/L)	Properties of the P3HT			
	%yield	%HT	λ_{\max}	M_n
0.69	85	74	437	27,656
0.35	89	72	439	- ^a
0.17	87	70	436	- ^a
0.11	80	69	436	17,087

^a not measured

3.1.4 Effect of the solvent

Among the tested solvent, the best solvent for the synthesis of P3HT was dichloromethane, giving the polymer at the highest yield of 94% and 78%HT (Table 3.4). 1,2-Dichloroethane gave a comparable result to dichloromethane with slightly less %HT. The other three solvents were all yielded inferior results: low %HT for toluene, low yield for CHCl_3 and cyclohexane. In the case of the latter solvent, the high M_n value contradicted its low λ_{\max} (Figure A-6, Appendix A), and all the results showed no correlation to the solvent polarity. The reason behind these results was yet unknown.

Table 3.4 Synthesis of P3HT prepared in a variety of solvent

solvent	Properties of the P3HT			
	%yield	%HT	λ_{\max}	M_n
CH_2Cl_2	94	78	440	20,018
$\text{C}_2\text{H}_4\text{Cl}_2$	94	73	436	17,228
toluene	93	64	430	11,566
CHCl_3	69	74	420	13,816
cyclohexane	86	72	422	32,574

3.1.5 Effect of the additives

During the previous experiments, we unexpectedly found that the polymer yields were varied when use differently aged anhydrous FeCl_3 reagent. The reason could arise from the varied amount of moisture gradually trapped by the reagent. We first tested this hypothesis by intentionally adding water into the reaction. The result clearly shown that the addition of water just only 2.5% of the weight of new anhydrous FeCl_3 gave worst values for all parameters of the properties of the obtained polymer (Table 3.5). Higher amount of water slowly degrade these properties, though not affected the yield.

Table 3.5 Synthesis of P3HT with addition of additives

additives	Properties of the P3HT			
	%yield	%HT	λ_{max}	M_n
none	94	78	440	20,018
2.5% H_2O	91	65	435	8,947
5% H_2O	90	63	429	7,266
10% H_2O	92	60	406	4,049
10% TFA	91	70	- ^a	- ^a
10% conc. H_2SO_4	87	69	- ^a	- ^a

^a not measured

From the proposed mechanism of polymerization reaction of 3-hexylthiophene to P3HT (Figure 3.2) the presence of water could generate cause hydroxide ions to accelerate the deprotonation from the coupled bithiophene intermediate and quickly rearomatization occurred irreversibly reaction (kinetic control) (Figure 3.3) Without water, the reaction could gradually reach the equilibrium where the intermediate towards HT is favored, (thermodynamic control) giving ratio of head-to-tail regiocouplings. Furthermore, water would also reduce the reactivity of the FeCl_3 reagent, resulting in less initiation and short chain length as reflected in lower M_n values.

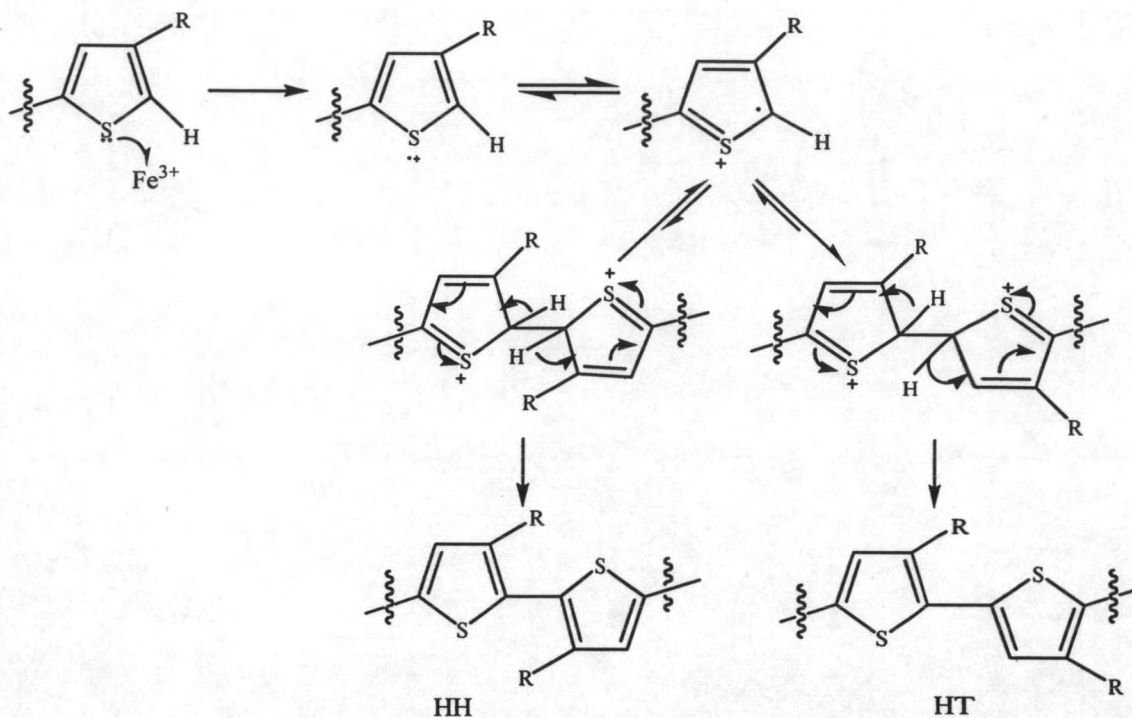


Figure 3.2 Mechanism of the two regiocouplings during the polymerization

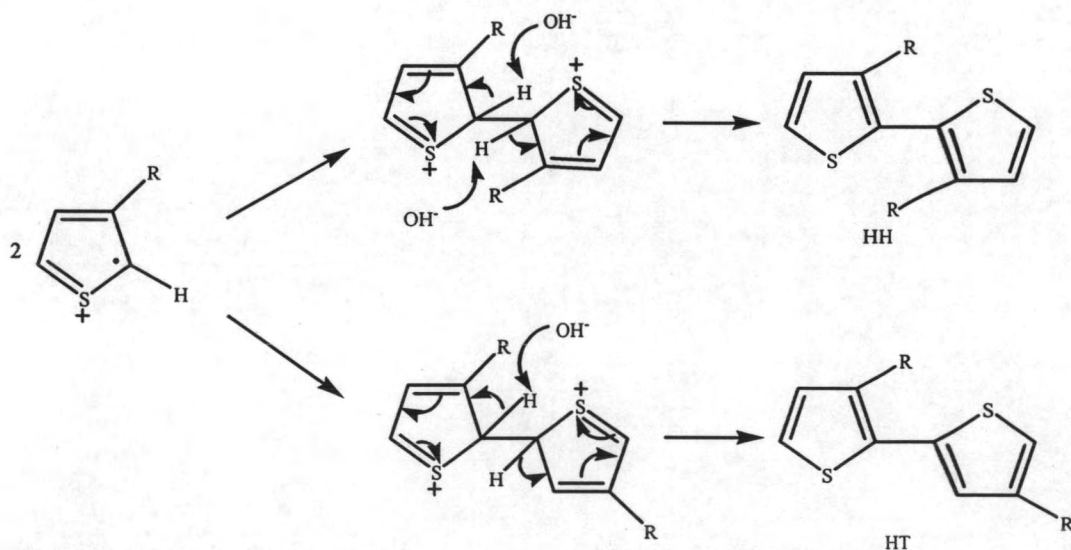


Figure 3.3 Mechanism of accelerated rearomatization of bithiophene units by hydroxide ions generated in the presence of water in the polymerization of 3-hexylthiophene

The tendency of the λ_{\max} decreased with the higher amount of water added (**Figure A-7**, Appendix A). It supported the result of %HT in which less %HT (or more steric HH) gave shorter conjugation length and made the two units of the polymer at HH junctions twisted from coplanar structures, resulting in decreasing the λ_{\max} values.

The other additives which generated less basic anions (trifluoroacetic acid and conc. sulfuric acid) than water gave the similar results in %yield but better in %HT. These results supported that weaker basic counter ions participated less in the from the thiophene rings. The results were still worse than the reaction with no additive in which, the even much less basic Cl^- would allow more HT coupling during the polymerization.

3.2. Fractionation of P3HT

3.2.1 Fractionation of P3HT obtained from general procedure

As-synthesized P3HT obtained from mole ratio of 3-hexylthiophene to ferric chloride equals 1:3 in section 3.1.1 was extracted sequentially with four solvents and separated into four fractions differing in their properties and molecular weight. The order of the solvent used in the extractions followed the report by Trznadel and coworkers [24]. The M_n value of each fraction was found to increase with the sequence of the extracting solvent. The M_n value of acetone fraction was lowest and its highest in the CHCl_3 fraction (**Table 3.6**). This result showed that the low molecular weight fraction containing shorter chain polymer was well soluble in acetone. The higher molecular weight polymer had poorer solubility and required the type of solvent with compromised range of polarity, such as CH_2Cl_2 and CHCl_3 .

Table 3.6 Macromolecular parameters of P3HT fractions from consecutive extractions

P3HT fractions	Parameters		
	wt%	λ_{\max} (nm)	M_n
acetone	32.94	372	2,514
hexane	15.29	413	11,794
CH ₂ Cl ₂	31.76	439	38,741
CHCl ₃	20.00	441	88,564
insoluble	trace	-	-

From the result of percentage of weight of P3HT, it showed two major components of the polymer distribution. 33% were short oligomers about the size of 15 repeating units. The other major part was extracted into CH₂Cl₂ fraction with average molecular weight of 38,741 (**Figure A-8**, Appendix A). The average molecular weights of all fractions were higher than that was reported by Trznadel and coworkers, in which their P3HT was synthesized from Grignard coupling reaction that is known to be of higher selectivity but lower in chain length than the oxidative coupling.

From the UV-visible spectra of each fraction of P3HT, redissolved in CHCl₃, they showed gradual bathochromic shifts of λ_{\max} (**Figure A-9**, Appendix A) with the increase of the average molecular weight of the polymer in the fractions (**Table 3.6**). The values seems to reach a plateau at approximately 441 nm and remain relatively unchanged even with substantially rise of molecular weight, as shown in the last two fractions. It is possible that the effective conjugation length of the polymer in this condition has reached its maximum and no longer depends on the size of the polymer chain.

3.2.2 P3HT obtained from the reactions with added water

As a continuation from the study on the effect of additives, (section 3.1.5) the polymers obtained from the reactions with additions of various amount of water were subjected to similar sequential extractions into four soluble fractions. It was found that the λ_{\max} values from UV-visible spectra of each fraction showed gradual bathochromic shift (Figure A-10 to A-13, Appendix A), which well corresponded to the possible longer effective conjugation length usually obtained with the longer polymer chain (Table 3.7).

Table 3.7 λ_{\max} values of P3HT obtained from the reactions with added water, separated into four fractions from consecutive extractions

P3HT fractions	λ_{\max} (nm)			
	0% H ₂ O	2.5% H ₂ O	5% H ₂ O	10% H ₂ O
acetone	372	390	<250	<250
hexane	413	426	399	388
CH ₂ Cl ₂	439	442	440	412
CHCl ₃	441	444	443	421

Table 3.8 Wt% of P3HT obtained from the reactions with added water, fractions from consecutive extractions

P3HT fractions	wt%			
	0% H ₂ O	2.5% H ₂ O	5% H ₂ O	10% H ₂ O
acetone	32.94	46.52	39.28	33.98
hexane	15.29	19.70	18.57	13.59
CH ₂ Cl ₂	31.76	24.98	21.43	29.21
CHCl ₃	20.00	08.53	04.28	02.17
Total	99.99	99.73	83.56	78.86
insoluble	00.01	00.27	16.44	21.14

From **Table 3.8**, the percentage weight of the CHCl_3 fraction decreased with added water. It was possible that water had decreased the effectiveness of the ferric chloride reagent and slowed down the polymerization process. This would yield polymer with lower molecular weight and more unreacted monomers or oligomers, which would not be precipitated by methanol after synthesis, yielding much less than 100% when combined all fractions together. (Total fractions, **Table 3.8**).

The insoluble parts of P3HT increased with percentage of added water (**Table 3.8**). It was suspected that this part might be mostly the insoluble ferric oxide or hydroxide, normally obtained from the reaction of FeCl_3 and water. To prove this hypothesis, the insoluble fractions were digested with boiling concentrated nitric acid. Ferric oxide was presumed to react with nitric acid and converted into water soluble nitrate salt that can be verified by UV-visible absorption.

The UV-visible spectra shown that the crude mixtures of P3HT and the insoluble parts of P3HT after digestions with nitric acid, gave the same spectra with the same λ_{max} at 301 nm, corresponding to the absorption of ferric ion in water. These observations supported the conclusion that crude mixtures and insoluble parts of P3HT that obtained from the reactions with wet FeCl_3 consisted of ferric oxide which was insoluble in organic solvents used in the extractions.

3.3 The doping of P3HT

3.3.1 Doping with protonic acids

From UV-visible spectra (**Figure A-14**, Appendix A) of TCA doped P3HT solution in CHCl_3 , the absorbances at higher wavelengths above 650 nm were all raised higher compared to the undoped solution. The absorption in this region normally reflected the presence of polaron that only occurred when the polymer was doped. The levels of those polaron absorption slightly increased with more acid added and no usual precipitation of the doped product, probably due to the still relatively low doping level.

AC-index value (**Figure 3.4** and **Table C-1**, Appendix C) can be calculated from the absorption data from **Figure A-14**. It was shown that

AC-index values increased quickly in the beginning and started to level off when TCA was added around 300 μmol (2.5 equivalent), which seemed to be the optimum doping level for this acid.

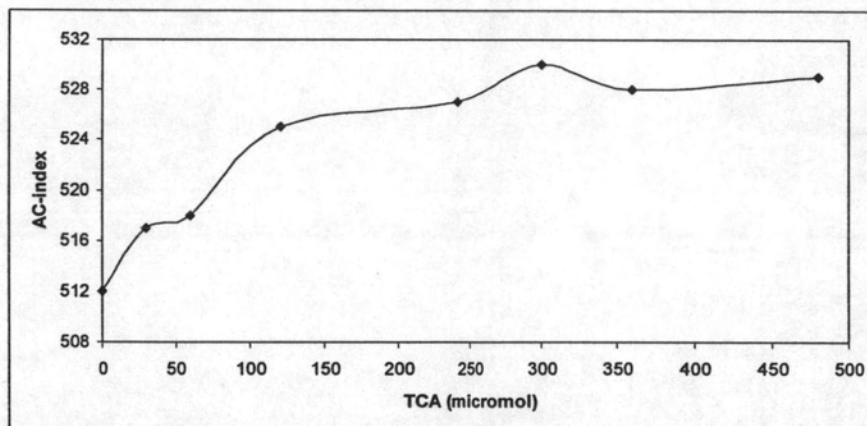


Figure 3.4 AC-index values of P3HT doped by various mole ratios of TCA

UV-visible spectra of TFA-doped P3HT solution in CHCl_3 (**Figure A-15**, Appendix A) show higher absorbances of the polaron than doping with TCA when the polymers were doped in the same condition. This should be from the fact that TFA is a stronger acid than TCA. AC-index value (**Table C-2**, Appendix C) of the polymer solution doped with TFA (120 μmol) were also (**Figure 3.5**) higher than polymer doped with TCA.

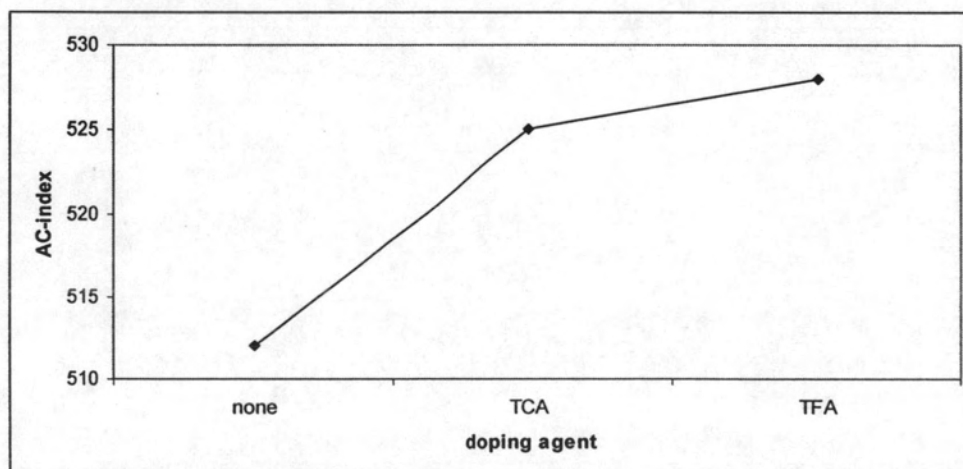


Figure 3.5 AC-index values of P3HT doped by TCA and TFA (120 μmol)

3.3.2 Doping with Lewis acids

All of Lewis acids in this study can dope P3HT, observed from the UV-visible spectra in which the polaron absorption regions were all slightly raised (**Figure A-16**, Appendix A) with an exception for $ZnCl_2$ where it has too low solubility in $CHCl_3$. Unfortunately, precipitation occurred during all the doping reactions. So they could not be cast into film. $FeCl_3$ can partly dissolve in $CHCl_3$ but immediately precipitated the P3HT upon doping. Most of the doped polymer seemed to be separated out of the solution and only the absorption of the $FeCl_3$ itself appeared in the UV-visible spectrum. $AlCl_3$ also partly dissolve in $CHCl_3$ and precipitated some of the polymer.

The UV-visible spectrum shown the usual absorption of the leftover P3HT and the slightly raised absorption in the polaron absorption region, suggesting that the doping reaction has occurred. $TiCl_4$ can doped the polymer and immediately precipitate the doped P3HT as well. The UV-visible spectrum shown that absorption of its polaron was slightly raised higher than that from $AlCl_3$ doping and no undoped P3HT was left in the solution.

3.3.3 Doping of P3HT film

The UV-visible spectra (**Figure A-17**, Appendix A) of the immersed P3HT film in MSA shown that the absorption at higher wavelengths including the region absorbed by polaron were clearly raised in the doped state. The length of time during the film immersion in the acid seemed not to make any differences in doping the polymer film (**Table C-3**, Appendix C). It is possible that the film was doped immediately when immersed in the acid and had already reached its maximum level.

3.4 Solvato-controlled doping

3.4.1 Varying mole ratios of MSA

From UV-visible spectra of doped P3HT film using various mole ratios of MSA as doping agent and thiophene as base (**Figure A-18**, Appendix A). The absorption in the polaron region was higher than that of the undoped film.

The AC-index values (Figure 3.6) (Table C-4, Appendix C) of doped film increased until the mole ratio of polymer:MSA:thiophene equaled 1:0.5:2 (Entry 2, Table 2.2) and started to decrease when more MSA was added, suggesting that the excess MSA directly doped P3HT solution and resulted in the precipitation of doped polymer before being cast into film.

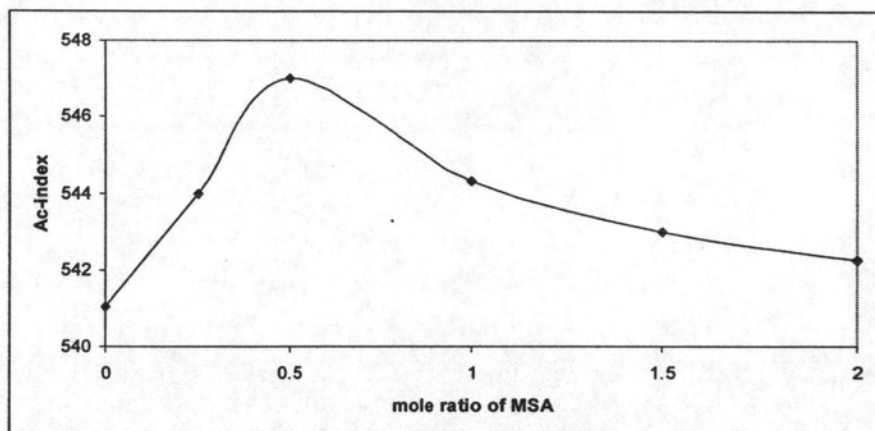


Figure 3.6 AC-index values of P3HT solvato-controlled doped by MSA and thiophene

3.4.2 Varying bases

The UV-visible spectra of P3HT doped with MSA and various bases (Figure A-19, Appendix A) shown that all bases gave the higher absorption in the polaron region. DMF gave the highest AC-index value (Figure 3.7) (Table C-5, Appendix C) but some salt was precipitated from the solution after evaporation of solvent. The precipitation of salt did not occur with thiophene as the ligand, although with lower AC-index value. Pyrrole and pyridine gave even lower AC-index values and also gave some precipitation of salt. These results suggested that DMF, pyrrole and pyridine were not appropriate to hold MSA, which resulted in the precipitation of salt.

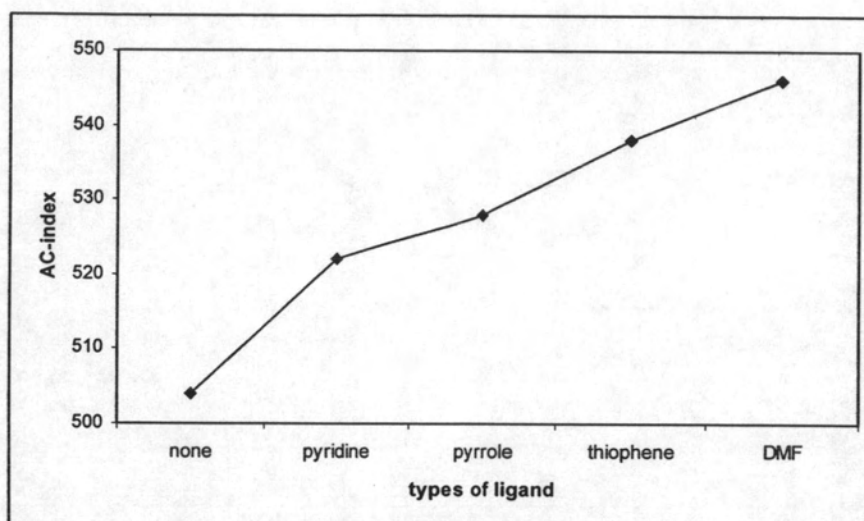


Figure 3.7 AC-index values of P3HT solvato-controlled doped by MSA and various bases

3.4.3 Varying ligands and Lewis acids

From various couples of doping agents and ligands, it was found that pyridine was the best ligand for the solvato-controlled doping condition using anhydrous FeCl_3 and AlCl_3 as doping agents (Entry 2 and 9, **Table 2.3**). Their AC-index values were, however, not very significant (**Figure A-20**, Appendix A; **Table C-6**, Appendix C and **Figure 3.8**).

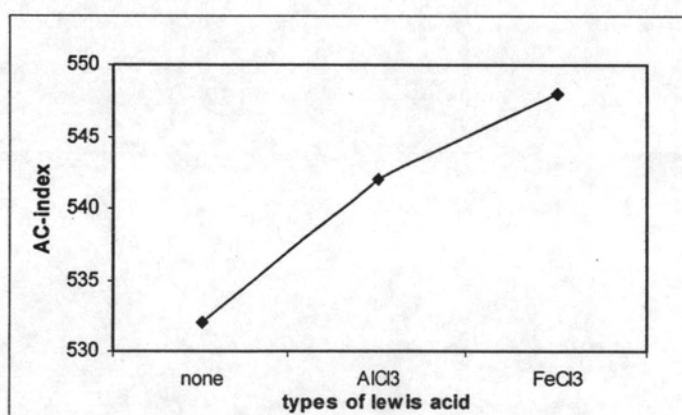


Figure 3.8 AC-index values of P3HT solvato-controlled doped by AlCl_3 and FeCl_3 with pyridine

Other pairs of Lewis acids and ligands in this study all gave precipitation of doped polymer (Entry 1,3,5,8,10,12,15-17, **Table 2.3**). Attempts to optimize the solvato-controlled doping by increase the amount of

AlCl_3 or FeCl_3 and pyridine ligand (Entry 4,6,7,11,13,14, **Table 2.3**) were not successful, only gave the precipitation of doped polymer as well.

4. Synthesis of copolymer

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the polythiophene derivatives with the highest conductivity, but insoluble in any solvent. Copolymerization of EDOT and 3-hexylthiophene in an appropriate amount could, in principle, give the polymer with higher conductivity than P3HT and still be made soluble in solvent for further processing. The current study, however, found that the copolymers from various mole ratios of EDOT and 3-hexylthiophene incompletely dissolved in CHCl_3 . The solubility of the resulting polymer decreased when increased the mole ratio of EDOT (**Table 3.9**).

Table 3.9 Properties of the copolymers prepared from various mole ratios of EDOT: 3-hexylthiophene

Mole ratios of EDOT:3-hexylthiophene	Properties of the copolymers			
	%yield	λ_{max} (nm)	M_n	%wt of soluble part in CHCl_3
75:25	103	422	718	28
50:50	102	438	12,406	57
25:75	92	441	13,378	88
0:100	94	440	20,018	100

The main reason could come from the difference in their reactivity. EDOT, with higher density of electrons than 3-hexylthiophene, was easier to be oxidized by FeCl_3 and subsequently polymerized to give PEDOT and precipitated from the solution before being incorporated into the much slower forming P3HT. The M_n values of the copolymer that was soluble and could be extracted into CHCl_3 decreased when more EDOT was added, supporting the earlier explanation that higher ratios of EDOT in the polymer chain caused the decrease of the solubility of the propagating polymer chain in the solvent and eventually precipitated the copolymer from the solvent prematurely as short chains. The soluble part of the copolymer mostly

contained the normal P3HT and perhaps some short-length copolymers that had less effective conjugation length and hence, decreased λ_{\max} values.

The $^1\text{H-NMR}$ spectra (Figure A-21, Appendix A) confirmed that the copolymer obtained from 25% EDOT and 75% 3-hexylthiophene contained only 7% by weight of EDOT in the largely P3HT chain (see Appendix B for calculation). The rest of the EDOT monomer probably polymerized into PEDOT and precipitated out of the solution.